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Low-energy elastic electron scattering by tetrafluoromethane (CF_4)

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We report cross sections for electronically elastic electron scattering by CF_4 from 1 to 40 eV, calculated within the static-exchange approximation using the Schwinger multichannel method. Although the static-exchange approximation does not give results that are accurate in detail below 20 eV, it is useful in understanding resonant features in the elastic and vibrationally inelastic cross sections. Above 20 eV, where the static-exchange approximation is more reliable, we derive a dissociation cross section in fair agreement with experiment by subtracting our result from the measured total cross section. We compare our integral and differential cross sections with the results of recent elastic and vibrationally inelastic scattering experiments.

I. INTRODUCTION

Low-energy electron scattering by tetrafluoromethane (CF_4) has been the subject of growing interest, primarily due to the importance of CF_4 as a feed gas in low-temperature plasmas used for "dry" etching of semiconductors. The modeling of such plasmas relies on knowledge of the relevant collision cross sections, including those for elastic electron scattering, vibrational excitation, and electron-impact dissociation to ions or neutral fragments. Considerable work has been done, mostly within the past decade, toward the elucidation of electron-CF_4 collision processes. However, the data are still incomplete and often inconsistent, and numerous aspects of the scattering remain puzzling.

Considering first electronically inelastic processes (all of which lead to dissociation), Winters *et al.*[1,2] have measured total electron-impact dissociation cross sections for CF_4. Märk *et al.*[3,4] and Ma *et al.*[5] have measured cross sections for electron-impact dissociation to ions, while quite recently Nakano and Sugai[6] have reported measurements of neutral-fragment (CF_3, CF_2, and CF) cross sections. The reliability of the inelastic cross sections can be judged by comparison with the difference between the total cross section[7–9] and the electronically elastic cross section. The latter can be obtained by summing the elastic cross section, which has recently been measured by Mann and Linder[10] and by Boesten *et al.*,[11] and the vibrationally inelastic cross section.[11,12] However, the integral elastic cross sections of Refs. 10 and 11 are quite different above 5 eV. This difference apparently arises from the extrapolation of the measured differential cross sections into the experimentally inaccessible forward- and backward-scattering regions, since the measured differential cross sections themselves are in good agreement. Consistency with the total scattering[7–9] and total dissociation[1,2] cross sections appears to favor the integral cross section of Ref. 11, but clearly an independent determination would be useful.

Calculations of elastic electron-CF_4 cross sections have been reported by Tossell and Davenport,[13] by Huo,[14] and by Baluja *et al.*[15] These results do not agree with each other, nor do any of them appear to be consistent with the inelastic and total scattering data at low energies. Further study is thus warranted. Here we report static-exchange calculations of the electron-CF_4 elastic scattering cross section. Since we are working in the fixed-nuclei approximation, neglecting nuclear dynamics, our results will best be compared with the electronically elastic, vibrationally summed cross section. Of the previous calculations, that of Huo[14] is most comparable to ours in that the fewest approximations have been made and that the Schwinger principle is used to obtain the scattering amplitude. However, our work incorporates certain computational improvements[16] that should lead to increased accuracy and employs a more extensive variational basis set, whose sufficiency has been tested by comparison with several other sets.

The static-exchange approximation has known deficiencies at the lowest energies, owing to its neglect of the target's response to the charge of the projectile; these usually take the form of a shift in resonance positions toward higher energies, typically by 2–4 eV, and of an artificially large *s*-wave scattering amplitude from about 0 to 5 eV. Nonetheless, because of the very regularity of their appearance, these effects can largely be discounted, and a fair understanding of the cross section, including an assignment of resonant features, can be extracted. Moreover, at higher energies, where polarization is less important, such calculations can be quantitatively reliable. It will be seen below that our results are in generally good agreement with the integral elastic cross section of Ref. 11 at higher energies, and in very good agreement with the differential cross sections of Refs. 10 and 11 at all but the lowest energies. Further, we will see that a fair approximation to the inelastic cross section above 20 eV can indeed be obtained by subtracting our calculated cross section from the total cross section, though limitations, to be discussed, do remain.

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The details of our calculation are given in the following section. Results are presented in Sec. III and discussed in Sec. IV.

II. CALCULATIONS

The Schwinger multichannel (SMC) method used in these calculations has been described elsewhere.[16–18] This method has recently been adapted to distributed-memory massively parallel computers,[19–21] facilitating accurate studies of scattering by larger molecules, and this parallel implementation was used in the present work. The main calculations were carried out on the Intel Touchstone DELTA system of the Concurrent Supercomputing Consortium (CSCC).

As noted earlier, we have worked in the fixed-nuclei static-exchange approximation. Other than the choice of this approximation, the principal limitation on the calculation is in the size and flexibility of the one-electron basis set that is used to describe the target orbitals and the scattering electron. We have tested a series of basis sets, including that of Ref. 14. The largest of these, comprising 198 primitive Gaussians contracted to 140 basis functions, was used for the results presented below. It consisted of the $4s2p$ C and $4s3p$ F basis sets of Dunning,[22] supplemented by one d function on C (exponent 0.8), and four p functions (exponents 0.12, 0.06, 0.03, and 0.015) and one d function (exponent 1.58) on F. Based on comparison with results obtained from smaller basis sets, we estimate that the cross section magnitude in this basis is converged to 10% or better over the energy range 1–40 eV, with the greatest uncertainty being directly on resonance and at the highest energies. In the latter case, the uncertainty is principally in the t_1 symmetry component, which is difficult to represent adequately. Our basis contains nine (threefold degenerate) molecular orbitals of t_1 type, of which one is occupied. It should be pointed out, moreover, that our basis set lacks any orbitals belonging to the a_2 irreducible representation of T_d, and the $^2A_2$ component of the cross section is therefore entirely absent.

The CF_4 target state was obtained in the self-consistent field (SCF) approximation at a C–F distance of 2.4944 atomic units. We calculated an SCF energy of −435.767 76 for ground state. All 119 virtual orbitals from the SCF calculation were used in constructing the scattering wave function.

III. RESULTS

Figure 1 shows the present static-exchange integral elastic cross section, along with the earlier theoretical cross section of Huo[14] and the experimental cross sections of Mann and Linder[10] and of Boesten *et al.*[11] For convenience in subsequent discussion, the total scattering cross section of Jones[8] is also shown. The broad double maximum that appears in our calculated result, but not in the experimental elastic cross sections, is probably associated with the broad peak near 9 eV in the total cross section, as will be discussed in the next section. The calculations of Tossell and Davenport[13] and of Baluja *et al.*[15] using more approximate methods do not give accurate results at these energies and are not shown in the figure.

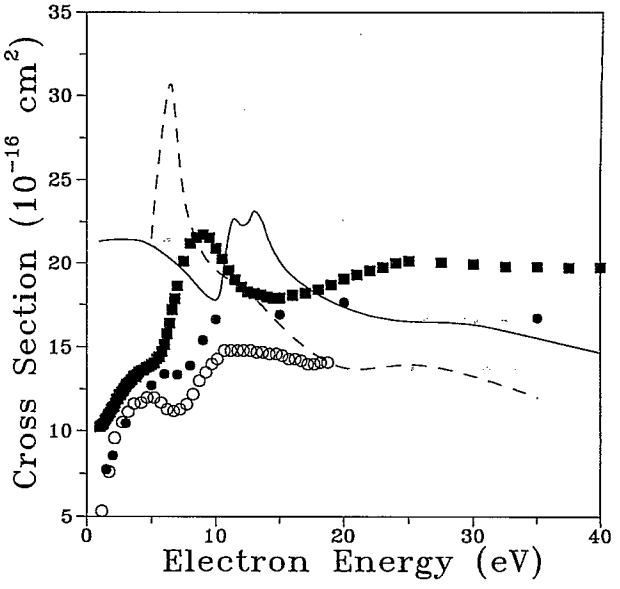

FIG. 1. Elastic electron scattering cross sections for CF_4. Solid line, present results; dashed line, calculation of Ref. 14; filled circles, experiment of Ref. 11; open circles, experiment of Ref. 10. Also shown for comparison is the total scattering measurement of Ref. 8 (filled squares).

Figure 2 shows the composition of our integral cross section in terms of contributions from different irreducible representations of T_d. The double maximum is seen to arise from closely-spaced peaks in T_2 and A_1 symmetries. There is also a shoulder in the E component near 26 eV. The large (spurious) s-wave contribution mentioned in Sec. I is seen as a steady rise in the $^2A_1$ component as the

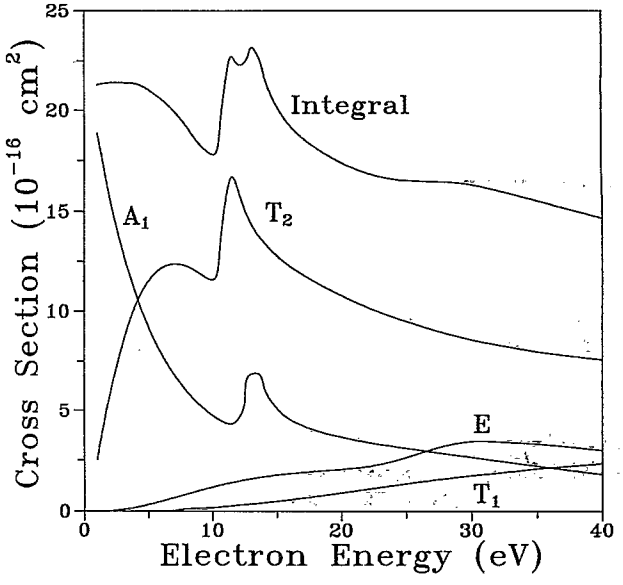

FIG. 2. Symmetry components of the electronically elastic scattering cross section for CF_4.

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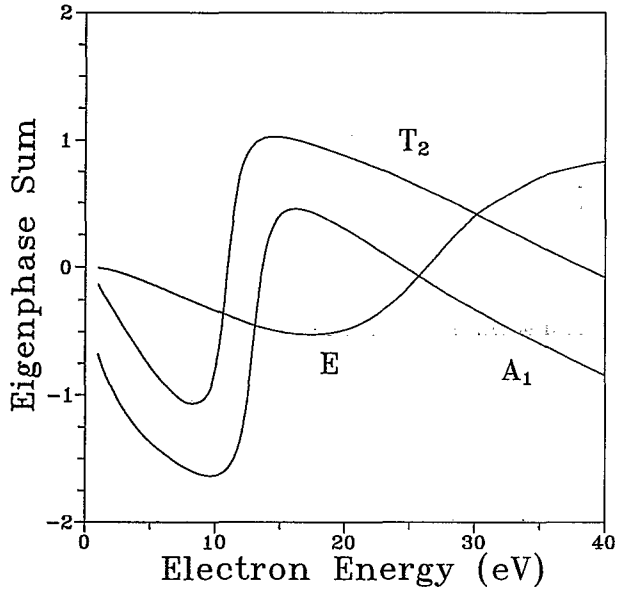

FIG. 3. Eigenphase sums for electron-CF_4 elastic scattering, showing T_2 and A_1 resonances and a possible broad E resonance near 26 eV.

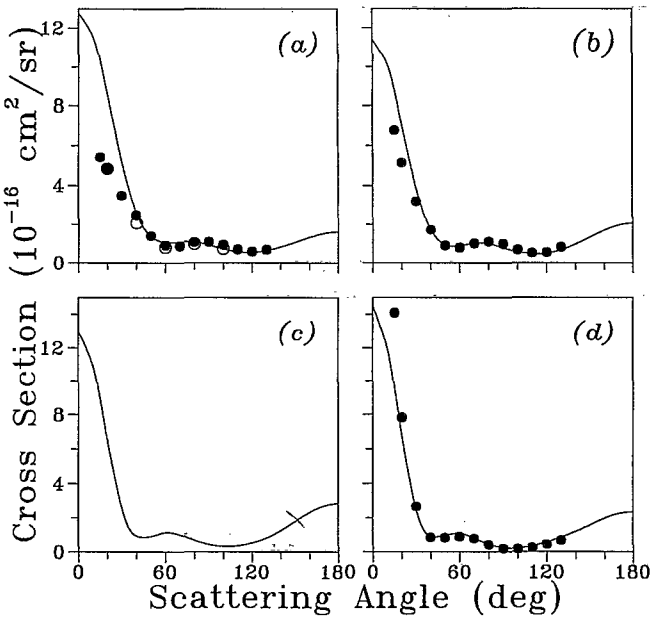

FIG. 5. As in Fig. 4, at (a) 15 eV; (b) 20 eV; (c) 28 eV; and (d) 35 eV.

impact energy goes to zero. Eigenphase sums for the different irreducible representations, Fig. 3, confirm the assignment of the T_2 and A_1 peaks as resonances, and indicate that the 26 eV shoulder in E symmetry arises from a broad resonance as well.

In Figs. 4 and 5, we show differential cross sections at selected energies, together with experimental results.[10,11] As is generally true for static-exchange calculations, the differential cross section is qualitatively incorrect at low energies but quite accurate at higher energies. From the differential cross sections, we obtain the momentum-transfer cross section, shown in Fig. 6 along with the experimentally-derived momentum-transfer cross section of Ref. 11. As in the integral cross section, we see resonant features not reflected in the experiment.

In Fig. 7, we show the electronically inelastic (total dissociation) cross section obtained by subtracting our fixed-nuclei static-exchange cross section from the experimental total cross section,[8] together with the measured total dissociation cross section.[1,2] At higher energies, where

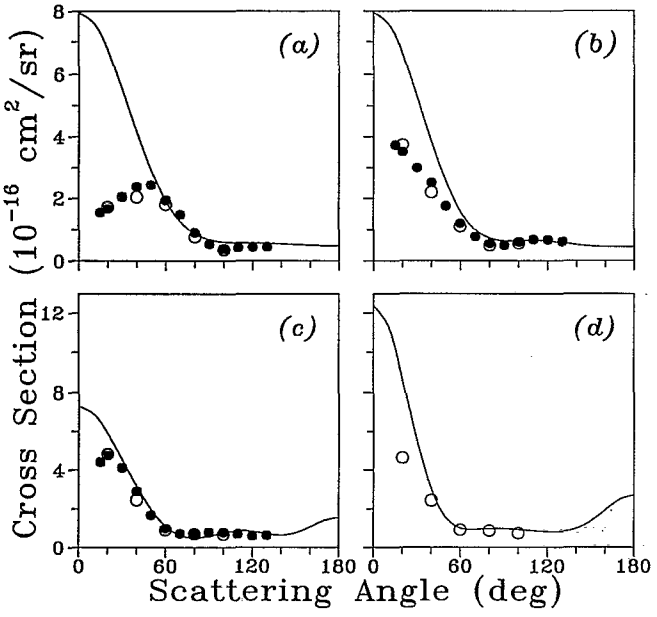

FIG. 4. Differential cross sections for elastic electron-CF_4 scattering at (a) 6 eV; (b) 8 eV; (c) 10 eV; and (d) 12 eV. Solid line, present results; filled circles, experiment of Ref. 11; open circles, experiment of Ref. 10.

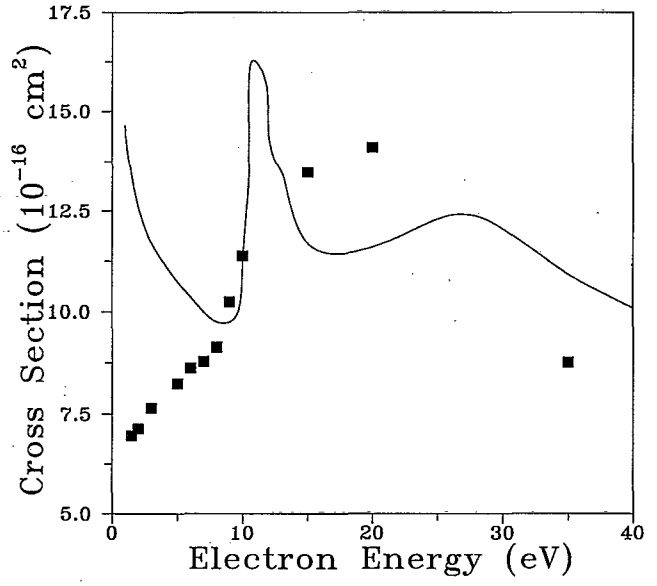

FIG. 6. Momentum-transfer cross section for electron-CF_4 scattering. Solid line, present results; circles, experiment of Ref. 11.

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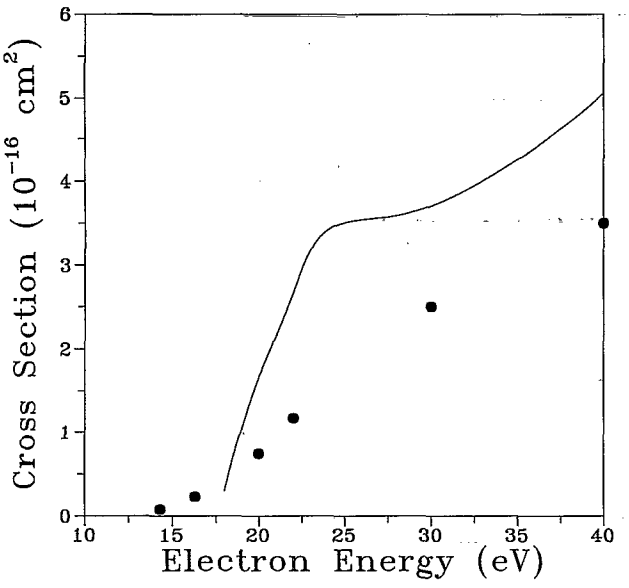

FIG. 7. Dissociation cross section for CF_4. Solid line is the value deduced from the present calculation and the total scattering data of Ref. 8; circles are experimental values of Refs. 1 and 2.

agreement should be best, we see that the results differ by ~50%, with the calculated value being larger. As will be discussed further, this difference is reasonable in light of the combined errors.

IV. DISCUSSION

As seen in Fig. 1, our results are considerably different from those of the only previous calculation of similar quality.[14] In particular, we find a different number of resonances and different resonance locations, and a substantially larger magnitude for the cross section at higher energies. We have used the same level of approximation in a more flexible basis, and it appears that these differences are due mostly to basis set limitations in the earlier study. In particular, we found it necessary to include more basis functions on the fluorine atoms, and to include additional diffuse functions, in order to obtain converged results. Differences in the treatment of matrix elements involving the Green's function[14,16] also appear to be important, however, since our results are somewhat different even when using the same basis set as Ref. 14. In contrast to Ref. 14, where an insertionlike quadrature was used, we have used numerical quadrature to evaluate these matrix elements. With such a quadrature representation of the Green's function,[16] the convergence of these matrix elements is easy to monitor, and we believe errors in our results arising from this source are on the order of a few percent at most.

The most remarkable feature of our calculated cross section is probably the broad double-peaked maximum around 12 eV (Fig. 1), which is absent from both experimental elastic cross sections. This maximum arises from closely-spaced resonances in T_2 and A_1 symmetry, located at ~11.5 and 13 eV, respectively (Fig. 2). The existence of such a pair of resonances, and the correct energy ordering, can in fact be inferred from the locations of the t_2 and a_1 σ^* virtual valence orbitals of CF_4.[23] Since, as discussed in Sec. I, the static-exchange approximation shifts resonances by 2–4 eV, we would expect from our calculation that resonant behavior be *observed* in the electronically elastic scattering at ~7.5–11 eV, which is indeed where a peak is seen in the total scattering cross section. Although the experimental integral cross section of Ref. 11 has shoulders at ~6 and 10 eV, the calculation can best be reconciled with the measurements on the assumption that almost all of the resonant scattering leads to vibrational excitation. Indeed, there is a great deal of evidence for strong vibrational excitation in this energy range, both based on swarm experiments[24] and direct observations of the vibrationally inelastic cross sections.[11,12] The strongest inelastic process is excitation of the ν_3 mode (asymmetric stretch), whose cross section has a peak at ~8 eV.[11,12] Symmetry analysis[11,12] indicates that excitation of ν_3 is consistent with a shape resonance in T_2 symmetry, and the shift of 3.5 eV between the calculated and experimental positions is quite reasonable. Similar considerations suggest that the A_1 resonance in the calculation, if not seen in the vibrationally elastic channel, should appear in the excitation cross section for the symmetric mode ν_1 at 9–11 eV. Mann and Linder[12] have tentatively deduced the presence of the A_1 resonance near 9 eV from a close analysis of the ν_1 contribution to their vibrational excitation data, in excellent agreement with the theoretically derived position. As pointed out in Ref. 12, these assignments are supported by dissociative attachment measurements,[25,26] which show two closely-spaced maxima in the cross section for production of F^- ions.

The remaining resonance feature indicated by the present calculations is the broad E resonance at ~26 eV. Boesten *et al.*[11] have observed a weak feature at 21 eV that they assign to T_2 symmetry. The assignment and the energy shift are both inconsistent with our 26 eV feature, since polarization should be fairly unimportant above 20 eV. We therefore do not believe the two features are related. The E resonance, being broad and weak, may be obscured by nonresonant scattering, although there is, in fact, a weak maximum in the total cross section at 25 eV,[7,8] near the calculated E resonance position. There is no indication of a second T_2 resonance in our results.

As seen in Fig. 7, the present results form the basis for a fair estimate of the dissociation cross section, though the error is considerable. One possible factor contributing to the error is the absence of basis functions of A_2 symmetry in the present work. Although such functions would only contribute to partial waves $l=6$ and higher in the scattering amplitude, an A_2 contribution on the order of 1×10^{-16} cm^2 at 40 eV, while small in comparison to the total elastic scattering, would account for most of the difference between the inelastic cross section obtained from the calculation and that measured by Winters *et al.*[1,2] The remaining difference may be ascribed to experimental error in the total scattering and total dissociation cross sections and to remaining uncertainties in the calculation, particularly in the T_1 scattering amplitude. Considering these lim-

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itations alongside the uncertainty inherent in extrapolating measured differential cross sections to 0° and 180° to obtain integral elastic cross sections, calculations at the static-exchange level appear able to offer an accuracy competitive with that of experiment for the purpose of deducing electronically inelastic cross sections.

In summary, we have presented calculated cross sections for the electronically elastic scattering of low-energy electrons by CF_4. Our results indicate the presence of overlapping T_2 and A_1 shape resonances that appear to be associated with maxima observed in the total scattering,[7–9] vibrational excitation,[11,12] and dissociative attachment[25,26] cross sections. At higher energies the present calculation forms the basis for a reasonable estimate of the dissociative excitation cross section. Quantitative calculations of cross sections below 20 eV will require the inclusion of polarization effects, both in order to obtain better resonance positions and to modify the *s*-wave scattering contribution. It would also be very interesting to account for nuclear motion, thus obtaining separate cross sections for the elastic and various inelastic vibrational channels. The present work should be useful as a point of reference in such studies.

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